Subcritical temperature in Bose - Einstein condensates of chiral molecules

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Bose-Einstein condensation of a sample of non-interacting chiral molecules leads to a non zero optical activity of the condensate and also to a subcritical temperature in the heat capacity. This is due to the internal structure of the molecule which, in our model, is considered as a simple two-state system, characterized by tunneling and parity violation. The predicted singular behavior found for the specific heat, below the condensation temperature, sheds some light on the existence of the so far elusive parity violation energy difference between enantiomers.

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Since the prediction and subsequent discovery of parity violation [1, 2] in weak interactions, the role of discrete symmetry breaking in fundamental physics is an intriguing field of research. Although the weak interaction (between electrons and nuclei) mediated by the gauge Z^0 boson has been extensively studied and observed in atoms [3], it has only been predicted in molecules. The importance of this symmetry-breaking in molecules is twofold: (i) it could be intimately related to the origin of homochirality, that is, the almost exclusive one-handedness of the chiral molecules found in living systems, this being one of the most fascinating open problems which links fundamental physics with the biochemistry of life [4] and (ii) at fundamental level, the intrinsic chiral nature which is present in some molecules should reflect the underlying interaction containing pseudoscalar magnitudes as those appearing in the weak one. In molecular systems, the theory of electroweak interactions predicts a parity violating energy difference (PVED) between the two enantiomers of chiral molecules to be between 10^{-13} and 10^{-21} eV [5–11]. However, no conclusive energy difference has been reported, for example, in experimental spectroscopic studies of the CHBrClF molecule reaching an energy resolution of about 10^{-15} eV [12, 13].

Due to the fact that the parity violating signals are easily masked by thermal effects, it is highly desirable to reach cold or ultracold regimes in the laboratory [14–17]. The measurement of fundamental physical properties such as the PVED between enantiomers could be achieved by trapping molecules at low temperatures (in the milikelvin range or below) and, subsequently, performing ultrahigh-resolution spectroscopic measurements of vibrational or electronic transitions. We would like to point out that these temperatures, and even colder, have been reached within the actual experimental capabilities only for atoms and diatomic molecules. The rapid expansion of the research field of ultracold chemistry is already opening new and exciting possibilities concerning more complex systems [18]. Thus, the study of quantum thermal effects in chiral molecules through pseudoscalar operators as the basic object describing their thermodynamics is of fundamental importance. Very recently, we have studied the corresponding classical thermodynamics of non-interacting chiral molecules [19, 20]. In this sense, as pointed out by Flambaum and coworkers concerning some capabilities of Bose-Einstein condensates to amplify weak interactions in chiral molecules [14], the study of Bose-Einstein condensation (BEC) for a gas of chiral molecules could shed some light on some properties relevant to determine the so far elusive PVED.

On the other hand, the study of cold atoms with intrinsic spin structure is being a very hot topic, including two-component condensates, spinor condensates, etc [21]. In this sense, for a Bose gas of chiral molecules, the inclusion of extra information about the internal structure of such molecules could be determinant to obtain some macroscopic properties relevant to determine the PVED such as, for example, by measuring the optical activity and heat capacity. For this end, we will employ a two-state model which includes tunneling and parity violating effects in chiral molecules (this approach was first considered in [22] and is widely used to describe, for instance, the internal dynamics of chiral molecules). Although the two-state (or spin 1/2) model is well known in many fields, including spin tunneling, magnetization, quantum dissipative systems, to name only a few, this is the first time, to the best of our knowledge, that this model is employed to study BEC of chiral molecules. Following the seminal works on BEC, predicted for a non-interacting gas and carried out in numerous dilute atomic gases [23] and in some diatomic molecules as in $^{40}K_2$ [24], we will assume that the interaction among molecules is negligible at first order and, therefore, a non-interacting quantum gas of chiral molecules will be considered.

In this Letter we show that a condensed gas of non-interacting chiral molecules displays optical activity. In addition, we show a dramatic change of the heat capacity with temperature, leading to the appearance of a secondary maximum (developing a shoulder-type-structure) associated with the Schottky anomaly below the condensation temperature. This *subcritical* temperature is expected to lie in the cold or ultracold regime.

In an ideal Bose-Einstein gas, only the translational part of the molecular motion is involved and the critical temperature for BEC is reached when the fugacity of the gas $z = \exp(\beta\mu)$, with μ being the chemical poten-

tial and $\beta = (k_B T)^{-1}$, is approaching unity (assuming that the energy of the ground state is zero) [25]. This T_c depends on the molecule mass and the density of the system. At $T < T_c$, there must be a non-negligible fraction of molecules in the ground state, the internal energy goes with $T^{5/2}$ and the heat capacity with $T^{3/2}$. If each chiral molecule in the condensed phase has its own internal structure, we could ask ourselves if the corresponding quantum statistics describing the thermodynamical behavior, intimately related to the PVED, can be manifested by a macroscopic effect. For this goal, a two-state model is assumed for each chiral molecule.

In the absence of parity violation, the dynamics of a chiral molecule is well described by a symmetric double well potential. In this case, the true stationary states of a chiral molecule are the (achiral) eigenstates of parity. The effect of including in the Hamiltonian the internal P-odd term given by the parity violating electron-nucleon electroweak interaction, H^{PV}, introduces an energy difference between the two minima of the double well potential, leading to a new set of energy eigenstates. Let us consider the total Hamiltonian of the system $H = H^0 + H^{PV}$, with H^0 including only parity conserving terms. Using a two-state model, we choose the left and right chiral states basis, $|L\rangle$ and $|R\rangle$ (localized respectively in the left and right minimum of the double well potential), in order to show clearly the parity properties of the Hamiltonian [22]:

$$H = H^0 + H^{PV} = \delta\sigma_x + \epsilon_{PV}\sigma_z \tag{1}$$

where $\sigma_{x,z}$ are the Pauli matrices. The eigenstates of H, $|1,2\rangle$, can be expressed as linear combinations of the chiral states by means of a rotation where the corresponding mixing angle, θ, obtained from the knowledge of the eigenvectors of H, is given by $\tan 2\theta = (2\,H_{LR}/H_{RR} - H_{LL}) = (\delta/\epsilon_{PV})$. The energy splitting between the two eigenstates of H^0 is $2\delta > 0$, where $\delta = \langle L|H^0|R\rangle$. This magnitude is related to the height of the barrier of the double well potential and is inversely proportional to the tunneling time. The PVED is then given by $|H_{RR} - H_{LL}| = |2\epsilon_{PV}|$ with $\epsilon_{PV} = \langle R|H^{PV}|R\rangle = -\langle L|H^{PV}|L\rangle$ (we remark that ϵ_{PV} is the eigenvalue of a pseudoscalar operator in the chiral basis). The eigenvalues of the system are given by $E_{1,2} = E_0 \mp \Delta$, with $E_0 = (H_{RR} + H_{LL})/2$ and $\Delta \equiv \sqrt{\epsilon_{PV}^2 + \delta^2}$ (hereafter we will take $E_0 = 0$ for the sake of simplicity).

Bose-Einstein condensation of a non-kinetic-two-state gas. In a gas of non interacting chiral molecules at temperature T, the inclusion of P-odd effects leads to deal with a pseudoscalar operator for obtaining any thermodynamic variable [19, 20]. Thus, for a system described by a biased double well potential, the only magnitude which, roughly speaking, distinguishes between left and right conformations is the population difference between both wells, $N_L - N_R$, which is directly related to the optical activity of the system. If X is a pseudoscalar operator, it can be shown that

$$|\langle X\rangle_{\rm stat}| = |x|\,(N_L - N_R)_{\rm stat}, \tag{2}$$

where $\pm x$ are the eigenvalues of X and the subscript *stat* stands for the different statistics considered. Eq. (2) is a generalization to any statistics of the Maxwell-Bolztmann (MB) thermal average [19]. A straightforward calculation gives the expression for $N_2 - N_1$ to be

$$(N_2 - N_1)_{\rm stat} = \tanh\beta\Delta\,(1 + p\,\frac{z + z^{-1}}{2}\,{\rm sech}\beta\Delta)^{-1}, \tag{3}$$

where $p = 0$ applies for MB, $p = -1$ for Bose-Einstein (BE) and $p = +1$ for Fermi-Dirac statistics. We remark that, when ϵ_{PV} dominates over δ, the true eigenstates of the system are the chiral states, $|L\rangle$ and $|R\rangle$, and changing the basis from $|1\rangle, |2\rangle$ to $|L\rangle, |R\rangle$ introduces the factor $\cos 2\theta = \epsilon_{PV}/\Delta$ leading to $N_L - N_R = \epsilon_{PV}(N_2 - N_1)/\Delta$. Moreover, $N_L - N_R$ changes its sign when considering a parity-transformed double well since ϵ_{PV} changes to $-\epsilon_{PV}$. From the knowledge of $N_2 - N_1$, the internal energy of the gas is

$$U = -\Delta(N_1 - N_2)_{\rm stat}. \tag{4}$$

From Eq. (4) one can inmediately obtain the heat capacity at constant volume. This C_v can be interpreted as a measure of the fluctuations of the optical activity of the system, that is, a measure of the fluctuations of the pseudoscalar character of the system.

Let us now consider BE statistics ($p = -1$) for a non-kinetic-two-state gas, that is, the Hamiltonian H includes tunneling and parity violation but not kinetic terms. The total number of particles is $N = N_1 + N_2$, where $N_{1,2}$ is the number of particles in the ground, $|1\rangle$, and the excited state, $|2\rangle$, respectively. Using the standard expression for the occupation numbers for Bose statistics, we get $N = N_1 + (z^{-1}\exp(\beta\Delta) - 1)^{-1}$. At the condensation temperature, T^*, all the particles are in the excited state, N_2. (this definition of the condensation temperature was also pointed out in [26]). This leads to the condensation temperature to be determined from

$$T^* = \frac{2\Delta}{k_B \ln(1 + \frac{1}{N})}. \tag{5}$$

The condensate displays a non-zero optical activity which is proportional to

$$N_2 - N_1 = 1 - 2\frac{\exp(2\beta^*\Delta) - 1}{\exp(2\beta\Delta) - 1}, \tag{6}$$

and this enables us to write, for $T < T^*$:

$$\frac{N_0}{N} = 1 - \frac{\exp(2\beta^*\Delta) - 1}{\exp(2\beta\Delta) - 1}, \tag{7}$$

the average internal energy as

$$u = \frac{U}{N} = \Delta(2\frac{\exp(2\beta^*\Delta) - 1}{\exp(2\beta\Delta) - 1} - 1), \tag{8}$$

and the heat capacity as

$$C_v = \frac{\partial u}{\partial T} = 4k_B(\beta\Delta)^2\frac{\exp(2\beta^*\Delta)}{\exp(2\beta\Delta) - 1}. \tag{9}$$

It is worth noting that this heat capacity reaches its maximum value at the *subcritical* temperature, T_{sc},

$$\beta_{sc}\Delta \simeq 0.797 \tag{10}$$

which reflects nothing but the Schottky anomaly due to the saturation of the energy levels of the system.

Bose-Einstein condensation of a kinetic-two-state gas. If we include a kinetic term in the Hamiltonian, the total partition function for an ideal Bose gas of chiral molecules in the two-state model can be written as

$$Z_{tot} = Z_{kin} \cdot Z_{int} \tag{11}$$

where the subscripts denote the kinetic and internal contributions, respectively. The first factor can be found in any standard textbook of Statistical Mechanics [25] and the second factor is given, for our case, by

$$Z_{int} = \prod_{i=1,2} (1 - z\, e^{-\beta E_i})^{-1}. \tag{12}$$

The factorization of the partition function leads to a sum of the corresponding heat capacities, $C_v^{tot} = C_v^{kin} + C_v^{int}$. We note that there are now two temperature regimes involved in the chiral system: (i) the temperature at which the gas undergoes BEC (T_c) and (ii) the *subcritical* temperature (T_{sc}, below T_c) where the heat capacity displays a maximum. In the case of a free gas, T_c is related to the mass and number density of the bosons but T_{sc} depends only (under the two-state model) on the energy splitting between $|1\rangle$ and $|2\rangle$ states. Thus, for $T < T_c$, C_v^{int} is given by Eq. (9) and, for $T > T_c$, the corresponding expression can be obtained from Eq. (4). C_v^{kin} is the usual heat capacity for an ideal Bose gas. It is worth pointing out that the very interesting case where T_c and T_{sc} are of the same order gives place to an appreciable change in the heat capacity and to a shoulder-type structure of it below T_c. This behavior is displayed in Fig. 1, where the total heat capacity is plotted in terms of the reduced temperature $k_B T/\Delta$ for the cases $T_{sc} = 0.1T_c$ (top panel) and $T_{sc} = 0.5T_c$ (bottom panel) (we have assumed $T^* = T_c$).

Strictly speaking, the effect of Δ on the condensation temperature, T_c, results into a very small shift. Thus for a kinetic-two-state-gas we get that the corrected or shifted condensation temperature is given by

$$\Upsilon = T_c \left(1 - \frac{\mathrm{cosech}\beta^*\Delta}{\mathrm{sech}\beta^*\Delta + e^{-3\beta^*\Delta} - 1} \right). \tag{13}$$

This difference is so tiny that for most practical purposes, we keep T_c instead of Υ.

When $T_c = T_{sc}$, the subcritical temperature corresponds to a very precise density of bosons of mass m, n_{sc}, given by

$$n_{sc} \simeq 0.178 \left(\frac{m\Delta}{\hbar^2} \right)^{3/2}. \tag{14}$$

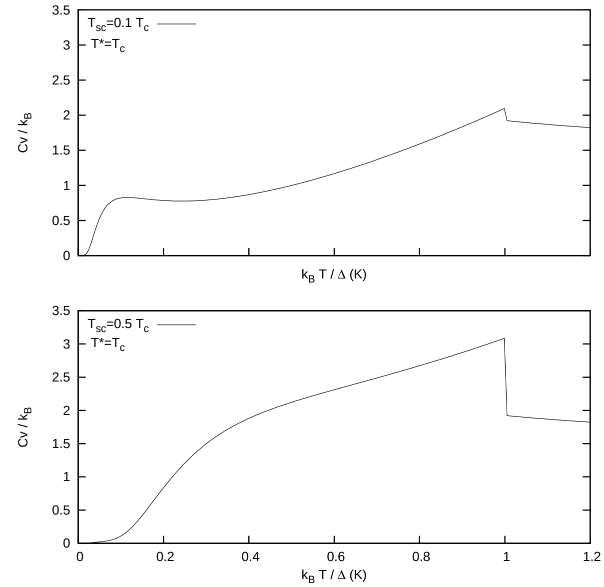

Figure 1. Total heat capacities for a gas of chiral molecules as a function of the reduced temperature for two cases: $T_{sc} = 0.1T_c$ and $T_{sc} = 0.5T_c$. The gas undergoes BEC at $k_BT/\Delta = 1$. We have taken $T^* = T_c$. See text for symbols.

The bottom panel of Fig. (1) should be observed, for example, for the T_2Se_2 system. This system has $\epsilon_{PV} \approx 2.5{\cdot}10^{-14}$ eV, $\delta \approx 5{\cdot}10^{-17}$ eV and the tunneling time is ~ 40 s (see Table 2 of [11]). Its subcritical density, n_{sc}, is about 10^{10} cm^{-3}, which is of the order of the critical densities. Thus, in this case, the corresponding discontinuity in the heat capacity could provide us a direct and clear signal of molecular parity violation.

In Fig. (2), a three dimensional plot of the heat capacity in the range of variation $[0, 1.2]$ of the reduced temperature and $[10^{-16}, 10^{-11}]$ of the splitting Δ (eV) is showed. In this plot it is clearly seen the overall shoulder-type structure as well as the subcritical maximum for different chiral molecules, characterized by the splitting Δ. This splitting is representative of molecules such as, for example, H_2S_2, CHBrClF and H_2Se_2 [11].

The subcritical maximum (or anomalous shoulder-type structure) found here could be considered as a signal of the Schottky anomaly which comes from lifting the degeneracy of the internal degrees of freedom. Although this was previously considered in the framework of a path integral approach to study BEC in spinor gases [27], our simple model allow us to identify more clearly the anomaly. We would like to stress that the *subcritical* temperature is determined in essence by δ and ϵ_{PV}, these temperatures lying in the cold or ultracold regime. The existence of that temperature could be possible for any system whose constituents have internal ground states slightly splitted, such as for example: the inversion doubling of non-rigid pyramidal molecules, the splitting due to torsional or internal rotations through potential barriers in non-rigid molecules, or eventually the hyperfine

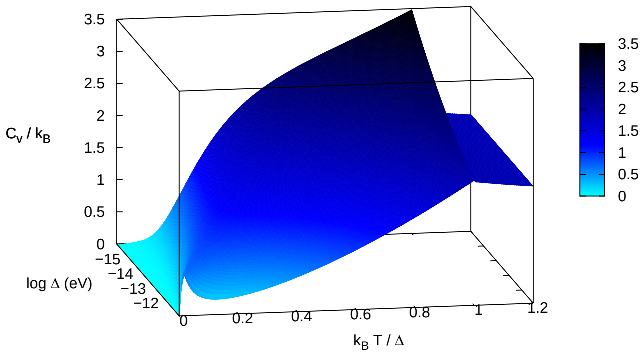

Figure 2. Three dimensional plot of the heat capacity versus Δ and the reduced temperature. The gas undergoes BEC at $k_BT/\Delta = 1$. We have taken $T^* = T_c$. See text for symbols.

structure of the ground state of atoms and molecules (in this last case, it could be more easy to verify the type of anomaly here studied). However, chiral molecules in this two-state model play a special role in BEC when the splitting is mainly due to parity violation (as in T_2Se_2). In this case, an observation of the anomaly predicted in the heat capacity provides a direct information about the PVED. In addition, when ϵ_{PV} determines the dynamics, then the eigenstates of the system tend to be the chiral states $|L, R\rangle$. We also point out that a measurement of the optical activity of the condensate would be a confirmation of the existence of the PVED, noting that the factor ϵ_{PV}/Δ, which is the optical activity for zero temperature, should be measurable by state-of-the-art of actual polarimeters, as we concluded in [20].

Finally, we would like to point out that the energy scale of molecular parity violation is associated with the natural scale of densities which corresponds to those achieved in Bose-Einstein condensates. Thus, BEC seems to be essential to detect the PVED. Furthermore, as is it well known, interactions could modify the physics of the problem so it is fundamental to ask ourselves to what extent the anomaly in the heat capacity persists when we consider an interacting system of chiral molecules. Although one could introduce the interaction between molecules under the Gross-Pitaevskii or any other more sophisticated treatment, an alternative way is to study the molecular sample as an open quantum system under the influence of dissipation. In this sense, we note that the heat capacity anomalies of open quantum systems have been recently studied when coupled to a thermal bath [28], showing the robustness of these anomalies when the interaction is taken into account. Thus, we expect that a similar stability for the anomaly here considered will persist even in presence of an environment. The study of heat capacity anomalies in BEC chiral gases embedded in appropiately chosen environments is currently in progress.

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[1] T. D. Lee and C. N. Yang, *Phys. Rev.*, **104**, 254 (1956).

[2] C. S. Wu *et al.*, *Phys. Rev.*, **105**, 1413 (1957).

[3] A.M. Bouchiat and C.C. Bouchiat, *Rep. Prog. Phys.*, **60**, 1351 (1997).

[4] A. Guijarro and M. Yus, *The Origin of Chirality in the Molecules of Life* (RSC Publishing, Cambridge, 2009).

[5] R. Zanasi, P. Lazzeretti, A. Ligabue and A. Soncini, *Phys. Rev. E*, **59**, 3382 (1999).

[6] J. K. Laerdahl, P. Schwerdtfeger and H. M. Quiney, *Phys. Rev. Lett*, **84**, 3811 (2000).

[7] J. Thyssen, J. K. Laerdahl and P. Schwerdtfeger, *Phys. Rev. Lett*, **85**, 3105 (2000).

[8] A. S. Lahamer *et al.*, *Phys. Rev. Lett*, **85**, 4470 (2000).

[9] P. Soulard *et al.*, *Phys. Chem. Chem. Phys.*, **8**, 79 (2006).

[10] D. Figgen and P. Schwerdtfeger, *Phys. Rev. A*, **78**, 012511 (2008).

[11] M. Quack, J. Stohner and M. Willeke, *Annu. Rev. Phys. Chem.*, **59**, 741 (2008).

[12] C. Daussy *et al.*, *Phys. Rev. Lett.*, **83**, 1554 (1999).

[13] J. Crassous *et al.*, *Org. Biomol. Chem.*, **3**, 2218 (2005).

[14] V. V. Flambaum and J. S. M. Ginges, *Phys. Rev. A*, **74**, 025601 (2006).

[15] P. Blythe, B. Roth, U. Frohlich, H. Wenz and S. Schiller, *Phys. Rev. Lett.*, **95**, 183002 (2005).

[16] J. M. Hudson and P. Soldan, *Int. Rev. Phys. Chem.*, **25**, 497 (2006).

[17] J. M. Hudson and P. Soldan, *Int. Rev. Phys. Chem.*, **26**, 1 (2007).

[18] L. D. Carr *et al.*, *New J. Phys.*, **11**, 055049 (2009).

[19] P. Bargueño *et al.*, *Chem. Phys. Lett.*, **486**, 204 (2009).

[20] I. Gonzalo *et al.*, *Chem. Phys. Lett.* **489** (2010) 127

[21] C. J. Pethick and H. Smith, *Bose-Einstein Condensation in Dilute Gases*, Cambridge University Press, 2002.

[22] R. A. Harris and L. Stodolsky, *Phys. Lett. B*, **78**, 313 (1978).

[23] M. H. Anderson *et al.*, *Science*, **269**, 198 (1995).

[24] C. A. Regal *et al.*, *Nature (London)*, **424**, 47 (2003).

[25] R. P. Feynman, *Statistical Mechanics*, Advance Books Classics, Addison-Wesley, 1998.

[26] W. Ketterle and N. J. van Druten, *Phys. Rev. A*, **54**, 656 (1996).

[27] L. F. Lemmens, F. Brosens and J. T. Devreese, *Phys. Rev. E*, **61**, 3358 (2000).

[28] G.-L. Ingold, P. Hänggi and P. Talkner, *Phys. Rev. E*, **79**, 061105 (2009).